

Alkoxylated Castor Oil

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(54) [Title of the Invention]

METHOD FOR MANUFACTURING POLYETHERS

(57) [Abstract]

[Purpose] To manufacture polyethers by taking castor oil compounds as initiators.

[Constitution] Polyether polyols with number average molecular weight of 3,000-5,000 and $M_w/M_n=1.3$ or less are manufactured by adding propylene oxide and/or ethylene oxide to 1,000 g polyols which are obtained by modifying castor oil, have 3-4 functional groups and hydroxyl value of 90-320 using zinc hexacyanocobaltate catalyst.

[Effects] The molecular weight and structure can be controlled.

[Claims]

[Claim 1] A method for manufacturing polyether, characterized by ring-opening polymerizations of monoepoxides having two or more carbons with castor oil and/or modified castor oils as initiators in the presence of bimetallic cyanide complex catalysts.

[Claim 2] The method of manufacturing polyethers of Claim 1 wherein the number average molecular weight of the resulting polyethers are 2,000-50,000.

[Claim 3] The method of manufacturing polyethers of Claim 1 wherein the weight average molecular weight/number average molecular weight (M_w/M_n) is 1.3 or less.

[Claim 4] The method of manufacturing polyethers of Claim 1 wherein said monoepoxides are alkylene oxides.

[Claim 5] The method of manufacturing polyethers of Claim 4 wherein said alkylene oxides are selected from ethylene oxide and propylene oxide.

[Detailed Explanation of the Invention]

[0001]

[Fields of Industrial Application] This invention is related to a method for manufacturing polyethers, in particular, to a method of manufacturing polyether polyols.

[0002]

[Previous Art] Polyethers such as polyoxyalkylene polyols obtained by ring-opening reactions of monoepoxides such as alkylene oxides with initiators, have been widely used as starting materials for synthetic resins such as polyurethane, surfactants, lubricants and other applications. The initiators are active hydrogen-containing compounds represented by $A-(H)_n$ (A: radicals obtained by removing hydrogen atoms of active hydrogen-containing compounds, and n: integrals of 1 or more).

[0003] As the initiators, for example, compounds having hydroxyl group(s) such as monohydroxy alcohols, polyhydroxy alcohols, monohydric phenol, polyhydric phenols, etc., and compounds having hydroxy-alkylamino group (alkanoamines or amine-alkylene oxide adducts, etc.), are given. The polyethers obtained by the monoepoxides with the above initiators are also used as initiators. Furthermore, attempts have been made to use castor oil and modified castor oil, such as ester-modified castor oil, as initiators.

[0004] The polyethers are the following compounds obtained by ring-opening addition reaction of monoepoxides with the above initiators.

A: $[-(R-O)_m-H]_n$

A: radicals obtained by removing hydrogen atoms of active hydrogen-containing compounds

R-O: ring-opened unit of monoepoxides

m, n: integrals of 1 or more

[0005] As previous methods of manufacturing polyethers, a method of reacting monoepoxides with initiators in the presence of alkali catalysts represented by alkali metal compounds, such as potassium hydroxide and sodium hydroxide, etc., has been widely used. Moreover, acid catalysts such as BF_3 etherate have also been used in the synthesis of low-molecular-weight polyethers.

[0006]

[Problems to Be Solved by the Invention] When castor oil compounds are used as initiators, the previously known alkali catalysts causes the decomposition of unsaturated and ester linkages contained in the castor oil compounds, therefore they cannot be used. If acid catalysts such as Lewis acids, etc. are used, high-molecular-weight polyethers are difficultly to be obtained.

[0007]

[Means of Solving the Problem] Because this invention should solve the above problems, it specifically is a method for manufacturing relatively high-molecular-weight polyethers by taking castor oil compounds as initiators. That is, this invention is a method of manufacturing polyethers, characterized by ring-opening addition reactions of monoepoxides having two or more carbon atoms in the presence of bimetallic cyanide complex catalysts by taking castor oil and/or modified castor oils as initiators.

[0008] The castor oil and modified castor oils are the natural oil obtained from castor seed and the modified castor oils obtained by treatments such as ester exchange, hydrogenation, sodium reduction reactions, etc. of said natural oil.

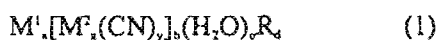
[0009] Castor oil is an unsaturated ester which takes ricinoleic acid as main component and is composed of glycerides of unsaturated acids. Its number of functional groups can be freely controlled by the ester exchange reaction.

[0010] The preferable monoepoxides having two or more carbons reacted with castor oil and/or modified castor oils in this invention are alkylene oxides with 3 or more carbons. More preferable are alkylene oxides with 3-4 carbons such as ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, epichlorohydrin, etc., and most preferable are ethylene oxide and propylene oxide.

[0011] These alkylene oxides can be used separately, and two or more of them, or their combinations with other monoepoxides such as styrene oxide, glycidyl ethers, glycidyl esters, etc. can be used. When two or more of alkylene oxides are used, or alkylene oxides and other monoepoxides are used, random polymerization chain or block polymerization chain can be formed by mixing and adding them or successively adding them.

[0012] It has been known to manufacture polyethers using the bimetallic cyanide complexes of this invention (USP 3,278,457, USP 3,278,458 and USP 3,278,458 Specifications). These catalysts make it possible to manufacture very high-molecular-weight polyethers with little formation of unsaturated mono-ols.

[0013] As shown by the above well-known examples, the bimetallic cyanide complexes in this invention are considered to have the structure of following general formula (1).



where M' is Zn(II), Fe(II), Fe(III), Co(II), Ni(II), Al(III), Sr(II), Mn(II), Cr(III), Cu(II), Sn(II), Pb(II), Mo(IV), Mo(VI), W(IV), W(VI), etc., M^2 is Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ni(II), V(IV), V(V), etc., R is organic ligands, a, b, x and y are positive integrals changed with atomicity and coordination number of metals, c and d are positive integrals changed with number of coordinating into metals.

[0014] For M' in general formula (1), Zn(II) is preferable, and for M^2 , Fe(II), Fe(III), Co(II), Co(III), etc. are preferable. As the organic ligands, for example, ketones, ethers, aldehydes, esters, alcohols, amides, etc., are given.

[0015] The bimetallic cyanide complexes represented by general formula (1), are manufactured by mixing respective aqueous solutions of metal salts $M'X_a$ (M' , a are same as above, and X is anions forming salts with M') and polycyanometalates (salts) $Z_e[M^2_x(CN)_y]_f$ (M^2 , x, y are same as above, Z is hydrogen, alkali metals, alkali-earth metals, etc., e, f are positive integrals decided by atomicity and coordination number of M^2) or their solutions in mixed solvents of water and organic solvents, contacting the organic ligands with the resulting bimetallic cyanides, and then removing excess solvents and organic ligands R.

[0016] For polycyanometalates (salts) $Z_e[M^2_x(CN)_y]_f$, various metals beginning with hydrogen and alkali metals can be used as Z, but lithium salts, sodium salts, potassium salts, magnesium salts and calcium salts are preferable, and common alkali salts, i.e. sodium salts and potassium salts are more preferable.

[0017] Both the polyethers having hydroxyl groups and polyisocyanate compounds are used as starting materials for manufacturing polyurethanes. These polyethers having hydroxyl groups are manufactured by adding monoepoxides, particularly alkylene oxides to polyhydroxy compounds, amine compounds and other initiators having at least one active hydrogen(s).

[0018] Alkali metal hydroxides such as potassium hydroxide, sodium hydroxide, etc., are most commonly used as catalysts in these addition reactions. Moreover, the use of such catalysts as boron trifluoride and tertiary amine, etc. has also been proposed.

[0019] When the monoepoxides are added to castor oil compounds taking as initiators, however, castor oil compounds have a problem of decomposition if the alkali catalysts are used. Moreover, they also have problems that high-molecular-weight polyethers are difficultly to be obtained and the molecular weight distribution of resulting polyethers is broadened if acid catalysts such as Lewis catalysts are used.

[0020] Because the bimetallic cyanide complex catalyst are used in this invention, the monoepoxides can be added to castor oil and/or modified castor oils takins as initiators. Moreover, the molecular weight can be controlled and relatively high-molecular-weight polyethers can be manufactured.

[0021] As methods of synthesizing relatively high-molecular-weight polyethers using common initiators but not using alkali or acid catalysts in addition to the method of using bimetallic cyanide catalysts, a method of using metal porphyrins has been known (Japan Kokai Tokkyo Koho S61-197631 (1986)), but when the metal porphyrins are used, the resulting polyethers have problems such as coloring, etc.

[0022] When the polyethers having hydroxyl groups manufactured by this invention are used as a starting material for polyurethane, the catalysts remained in the polyethers exert bad influences on the ractions in the manufacture of polyurethane or on the physical properties of the produced polyurethane. It is preferable to remove the remained catalysts after the manufacture of polyethers.

[0023] In order to remove the catalysts from the polyethers obtained by using bimetallic cyanide complex catalysts, it is necessary not only to treat them by simple filtration or with adsorbents, etc., but also to remove them by decomposition and ionization of the catalysts with alkalis or acids, then adsorption, filtration, extraction, etc. of these decomposition products, remained alkalis or acids.

[0024] As methods of decomposing and removing the catalysts, a method of decomposition with alkali metals or alkali metal compounds (Japan Tokkyo Koho S59-15336 (1984), a method of decomposition with alkali metal alcoholates (Japan Kokai Tokkyo Koho H2-276821 (1990), a method of decomposition and removal with pH buffering agents or a combination of pH buffering agents and chelating agents (Japan Kokai Tokkyo Koho H2-289617 (1990), Japan Kokai Tokkyo Koho H2-289618 (1990)) have been discovered. The method of using pH buffering agents is suitable for removing the catalysts from polyethers of this invention.

[0025] The number-average molecular weight of polyethers having hydroxyl groups obtained in this invention preferably is 2,000-50,000, and more preferably 2,000-30,000.

[0026] Moreover, the polyethers having hydroxyl groups obtained in this invention preferably have small values of weight average molecular weight/number average molecular weight (taken as M_w/M_n below). M_w/M_n of 1.3 or less is more preferable.

[0027] Castor oil and modified castor oils of this invention have hydroxyl groups, and under certain circumstance, have carboxyl group. If the bimetallic cyanide complex catalysts are used, the monoepoxides can be added to the both functional groups. The polyethers thus obtained have only end hydroxyl groups.

[0028] The polyethers having hydroxyl groups obtained by this invention, used separately or in combination with other polyols, are the most useful as polyether polyols for starting materials of polyurethanes. Moreover, the polyethers obtained by this invention are also used as starting materials and additives of synthetic resins other than polyurethanes. Furthermore, they can be used as lubricants, insulating oils, hydraulic oils and other oils, or as their starting materials. Still more, the polyethers obtained by this invention can be changed into other compounds such as alkyl etherates, acylates, etc. for various purposes.

[0029]

[Examples] The addition reactions of alkylene oxides with the following castor oil initiators were carried out using various catalysts.

Initiator A: a polyol having 3 functional groups and hydroxyl value of 160 obtained by a modifying castor oil (URIC H-30, made by Ito Oil Manufacture Co.)

Initiator B: a polyol having 3 functional groups and hydroxyl value of 90 obtained by a modifying castor oil (URIC H-57, made by Ito Oil Manufacture Co.)

Initiator C: a polyol having 4 functional groups and hydroxyl value of 320 obtained by a modifying castor oil (URIC H-91)

[0030] [Example 1] 1,920 g propylene oxide was added to 1,000 g initiator A at 110°C using 200 ppm zinc hexacyanocobaltate (with respect to finished product) to give a polyether polyol.

[0031] [Example 2] 1,700 g 70/30 wt% mixture of propylene oxide and ethylene oxide was reacted with 1,000 g initiator B at 105°C using 253 ppm zinc hexacyanocobaltate (with respect to finished product), the resulting polyol was treated with ammonia, then adsorption treated with synthetic magnesium silicate and filtered to give a polyether polyol.

[0032] [Example 3] 1,000 g propylene oxide, followed by 3,800 g mixture of 40/60 wt% propylene oxide/ethylene oxide, were reacted with 1,000 g initiator C at 110°C using 250 ppm zinc hexacyanocobaltate (with respect to finished product), the resulting polyol was treated with

ammonia, then adsorption treated with synthetic magnesium silicate and filtered to give a polyether polyol.

[0033] [Example 4] Propylene oxide was reacted with 1,000 g initiator A using 2,000 ppm potassium hydroxide as catalyst (with respect to finished product) in the same manner as in Example 1, then adsorpted treated with synthetic magnesium silicate to give a polyether polyol.

[0034] [Example 5] The mixture of propylene oxide and ethylene oxide was reacted with 1,000 g initiator B using 2,000 ppm BF_3 etherate (with respect to finished product) in the same manner as in Example 2, then adsorption treated with synthetic magnesium silicate to give a polyether polyol.

[0035] [Example 6] Propylene oxide and ethylene oxide were reacted with 1,000 g initiator C using 3,000 ppm potassium hydroxide as catalyst (with respect to finished product) in the same manner as in Example 3, then adsorption treated with synthetic magnesium silicate to give a polyether polyol. The properties of polyether polyols obtained in Examples 1-6 are shown in Table 1.

[0036]

[Table 1]

| | | Appearance | Hydroxyl Value | M_w/M_n |
|-----------|-----------|--------------|----------------|-----------|
| Example | Example 1 | clear | 56.3 | 1.10 |
| | Example 2 | clear | 33.2 | 1.12 |
| | Example 3 | clear | 56.0 | 1.13 |
| Comarison | Example 4 | dark brown | 82.5 | 1.7 |
| Example | Example 5 | gained black | 80.0 | 1.8 |
| | Example 6 | dark brown | 70.2 | 1.75 |

[Effects of the Invent] This invention is a method of manufacturing polyethers by taking castor oil compounds as initiators. The free control of molecular weight and structure which was previously impossible, is achieved.